

Analytical Methods
Semivolatile Organic Extractions
3510C/3550B

METHOD 3510C

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel.

2.2 The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Method 3510 is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520, and performing the initial extraction at the acid pH.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.7 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

4.8 pH indicator paper - pH range including the desired extraction pH.

4.9 Erlenmeyer flask - 250-mL.

4.10 Syringe - 5-mL.

4.11 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.4 Sodium sulfate (granular, anhydrous), Na₂SO₄. Purify by heating to 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.5 Sulfuric acid solution (1:1 v/v), H₂SO₄. Slowly add 50 mL of H₂SO₄ (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

5.6.1 Methylene chloride, CH₂Cl₂, boiling point 39°C.

5.6.2 Hexane, C₆H₁₄, boiling point 68.7°C.

5.6.3 2-Propanol, CH₃CH(OH)CH₃, boiling point 82.3°C.

5.6.4 Cyclohexane, C₆H₁₂, boiling point 80.7°C.

5.6.5 Acetonitrile, CH₃CN, boiling point 81.6°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sect. 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample. Alternatively, if the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used.

7.2 Pipet 1.0 mL of the surrogate spiking solution into each sample in the graduated cylinder (or sample bottle) and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and matrix spiking solution).

7.2.1 For the sample in each batch (see Chapter One) selected for use as a matrix spike sample, add 1.0 mL of the matrix spiking standard.

7.2.2 If Method 3640, Gel-Permeation Cleanup, is to be employed, add twice the volume of the surrogate spiking solution and the matrix spiking standard, since half of the extract is not recovered from the GPC apparatus. (Alternatively, use 1.0 mL of the spiking solutions and concentrate the final extract to half the normal volume, e.g., 0.5 mL instead of 1.0 mL).

7.3 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1, using 1:1 (v/v) sulfuric acid or 10 N sodium hydroxide. Lesser strengths of acid or base solution may be employed, provided that they do not result in a significant change (<1%) in the volume of sample extracted (see Secs. 5.3 and 5.5).

7.4 Quantitatively transfer the sample from the graduated cylinder (or sample bottle) to the separatory funnel. Use 60 mL of methylene chloride to rinse the cylinder (or bottle) and transfer this rinse solvent to the separatory funnel. If the sample was transferred directly from the sample bottle, refill the bottle to the mark made in Sec. 7.1 with water and then measure the volume of sample that was in the bottle.

7.5 Seal and shake the separatory funnel vigorously for 1 - 2 minutes with periodic venting to release excess pressure. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

7.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.7 Repeat the extraction two more times using fresh portions of solvent (Secs. 7.2 through 7.5). Combine the three solvent extracts.

7.8 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Secs. 7.2 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.9 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.10 Perform the concentration (if necessary) using the Kuderna-Danish Technique (Secs. 7.11.1 through 7.11.6).

7.11 K-D technique

7.11.1 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11.2 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.11.3 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.11.5 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4. Concentrate the extract, as described in Sec. 7.11.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11.6 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2) is used to adjust the extract to the final volume required.

7.12.1 Micro-Snyder column technique

If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or the exchange solvent, and adjust the final volume as indicated in Table 1, with solvent.

7.12.2 Nitrogen blowdown technique

7.12.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce contaminants.

7.12.2.2 The internal wall of the tube must be rinsed several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a PTFE-lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Deter- minative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL) ^a
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5 ^b
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270 ^{c,d}	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

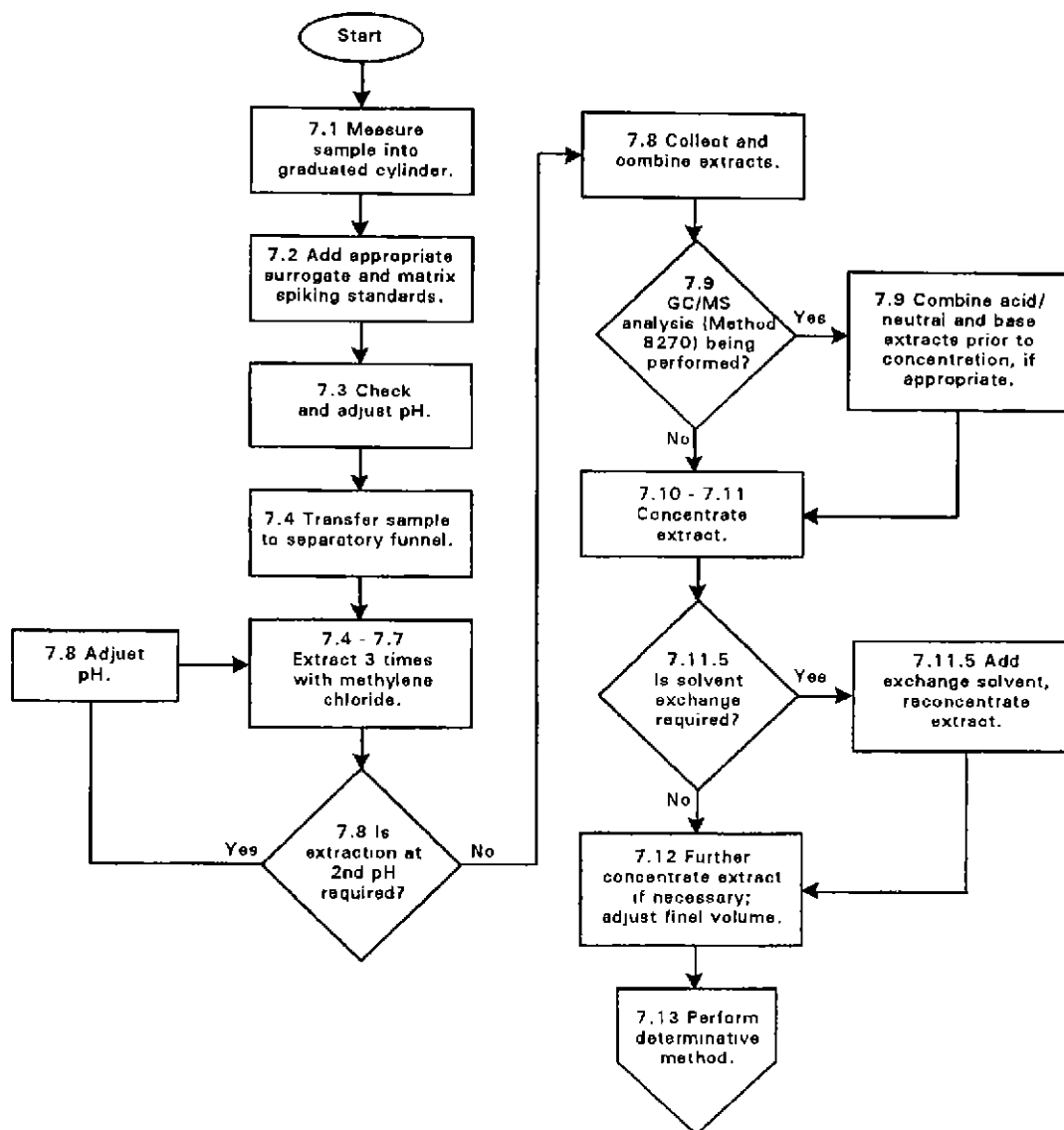
^a For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

^b Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.

^c The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

^d Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).

METHOD 3510C
SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION



METHOD 3550B

ULTRASONIC EXTRACTION

See Disclaimer. See manufacturer's specifications for operational settings.

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of less than or equal to 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Sec. 4.2.2, for applicable methods.

1.4 Ultrasonic extraction is not as rigorous as other extraction methods for soils/solids. Therefore, it is critical that the method (including the manufacturer's instructions) be followed explicitly in order to achieve the maximum extraction efficiency. See Sec. 7.0 for the critical aspects of the extraction procedure.

1.5 EPA has not validated Method 3550 for the extraction of organophosphorous compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorous compounds (see Reference 3). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 This method is not appropriate for applications where high extraction efficiencies of analytes at very low concentrations is necessary (e.g., demonstration of effectiveness of corrective action).

2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 Medium/high concentration method - A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

4.2.2 Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

4.3 Sonobox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent dry weight.

4.4.1 Drying oven - capable of maintaining 105°C.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1-mL, disposable.

4.6 Beakers - 400-mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.9 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.10 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.11 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.12 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.

4.13 Vials - 2-mL, for GC autosampler, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

4.15 Spatula - Stainless steel or PTFE.

4.16 Drying column - 20-mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.17 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall conform to the specifications of the Committee on

Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix. Table 1 provides recovery data for selected semivolatile organic compounds extracted from an NIST SRM. The following sections provide guidance on the choice of solvents for various classes of analytes. All solvents must be pesticide quality or equivalent.

5.4.1 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$ or acetone/hexane (1:1, v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$.

5.4.2 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$ or acetone/methylene chloride (1:1, v/v), $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$.

5.4.3 PCBs may be extracted with acetone/hexane (1:1, v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$, acetone/methylene chloride (1:1, v/v), $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$ or hexane, C_6H_{14} .

5.4.4 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix (see Method 3500, Sec. 8.0).

5.5 Exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Hexane, C_6H_{14} .

5.5.2 2-Propanol, $(\text{CH}_3)_2\text{CHOH}$.

5.5.3 Cyclohexane, C_6H_{12} .

5.5.4 Acetonitrile, CH_3CN .

5.5.5 Methanol, CH_3OH .

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

As noted in Sec. 1.4, ultrasonic extraction is not as rigorous a method as other extraction methods for soils/solids. Therefore, it is critical that the method be followed explicitly (including the manufacturer's instructions) to achieve the maximum extraction efficiency. At a minimum, successful use of this technique requires that:

- The extraction device must have a minimum of 300 watts of power and be equipped with appropriate size disrupter horns (see Sec. 4.2).
- The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.
- The samples must be properly prepared by thorough mixing with sodium sulfate so that it forms a free-flowing powder prior to the addition of the solvent.
- The extraction horns used for the low concentration and high concentration protocols (Sec. 7.3 and Sec. 7.4, respectively) are not interchangeable. Results indicate that the use of the 3/4" horn is inappropriate for the high concentration method, particularly for extraction of very non-polar organic compounds such as PCBs, which are strongly adsorbed to the soil matrix.
- Three extractions are performed with the appropriate solvent, the extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
- Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. The analyst must observe such mixing at some point during the extraction process.

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This extraction procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

7.2 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides (less than or equal to 20 mg/kg):

7.3.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.3.1.1 Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.

7.3.1.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

7.3.1.3 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of surrogate compounds and concentrations.

7.3.1.4 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of matrix spiking compounds and concentrations.

7.3.1.5 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.3.1.6 Immediately add 100 mL of the appropriate/recommended extraction solvent or solvent mixture (see Sec. 5.4 and Table 1).

7.3.2 Place the bottom surface of the tip of the #207 (or equivalent) 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

NOTE: Be sure the horn is properly tuned according to the manufacturer's instructions.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

7.3.4 Decant the extract and filter it through Whatman No. 41 filter paper (or equivalent) in a Buchner funnel that is attached to a clean 500-mL filtration flask. Alternatively, decant the extract into a centrifuge bottle and centrifuge at low speed to remove particles.

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 7.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the Kuderna-Danish apparatus following manufacturer's instructions. Transfer filtered extract to a 500-mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation flask, and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Sec. 7.3.10, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 - 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.3.10 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.3.10.1) or nitrogen blowdown technique (Sec. 7.3.10.2) may be used to adjust the extract to the final volume required.

7.3.10.1 Micro Snyder column technique

7.3.10.1.1 Add a clean boiling chip and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the

water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.3.10.2 Nitrogen blowdown technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample, since it may introduce contaminants.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 Extraction method for samples expected to contain high concentrations of organics (greater than 20 mg/kg):

7.4.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.4.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.4.3 Surrogates are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate spiking solution and on the matrix spike solution).

7.4.3.1 Add 1.0 mL of surrogate spiking solution to sample mixture.

7.4.3.2 For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard.

7.4.3.3 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.4.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

7.4.4.1 For nonpolar compounds (i.e., organochlorine pesticides and PCBs), use hexane or appropriate solvent.

7.4.4.2 For other semivolatile organics, use methylene chloride.

7.4.5 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the sample extract through the glass wool and collect the extract in a suitable container. The entire 10 mL of extraction solvent cannot be recovered from the sample. Therefore, the analyst should collect a volume appropriate for the sensitivity of the determinative method. For instance, for methods that do not require that the extract be concentrated further (e.g., Method 8081 typically employs a final extract volume of 10 mL), the extract may be collected in a scintillation vial or other sealable container. For extracts that will require further concentration, it is advisable to collect a standard volume for all such samples in order to simplify the calculation of the final sample results. For instance, collect 5.0 mL of extract in a clean concentrator tube. This volume represents exactly half of the total volume of the original sample extract. As necessary, account for the "loss" of half of the extract in the final sample calculations, or concentrate the final extract to one-half the nominal final volume (e.g., 0.5 mL vs. 1.0 mL) to compensate for the loss.

7.4.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

7.5 If analysis of the extract will not be performed immediately, stopper the concentrator tube and refrigerate. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, and replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

2. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes from Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.
3. Kotronarou, A., et al., "Decomposition of Parathion in Aqueous Solution by Ultrasonic Irradiation," *ES&T*, 1992, Vol. 26, 1460-1462.

TABLE 1
EFFICIENCIES OF VARIOUS EXTRACTION SOLVENT SYSTEMS^a

Compound	CAS No. ^b	ABN ^c	Solvent System ^d									
			A		B		C		D		E	
			%R	SD	%R	SD	%R	SD	%R	SD	%R	SD
4-Bromophenyl phenyl ether	101-55-3	N	64.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
Bis(2-chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
Bis(2-chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-o-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	62.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-o-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

^a Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645

^b Chemical Abstracts Service Registry Number

^c Compound Type: A = Acid, B = Base, N = neutral

^d Solvent system A = Methylene chloride

Solvent system B = Methylene chloride/Acetone (1/1)

Solvent system C = Hexane/Acetone (1/1)

Solvent system D = Methyl t-butyl ether

Solvent system E = Methyl t-butyl ether/Methanol (2/1)

TABLE 2
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

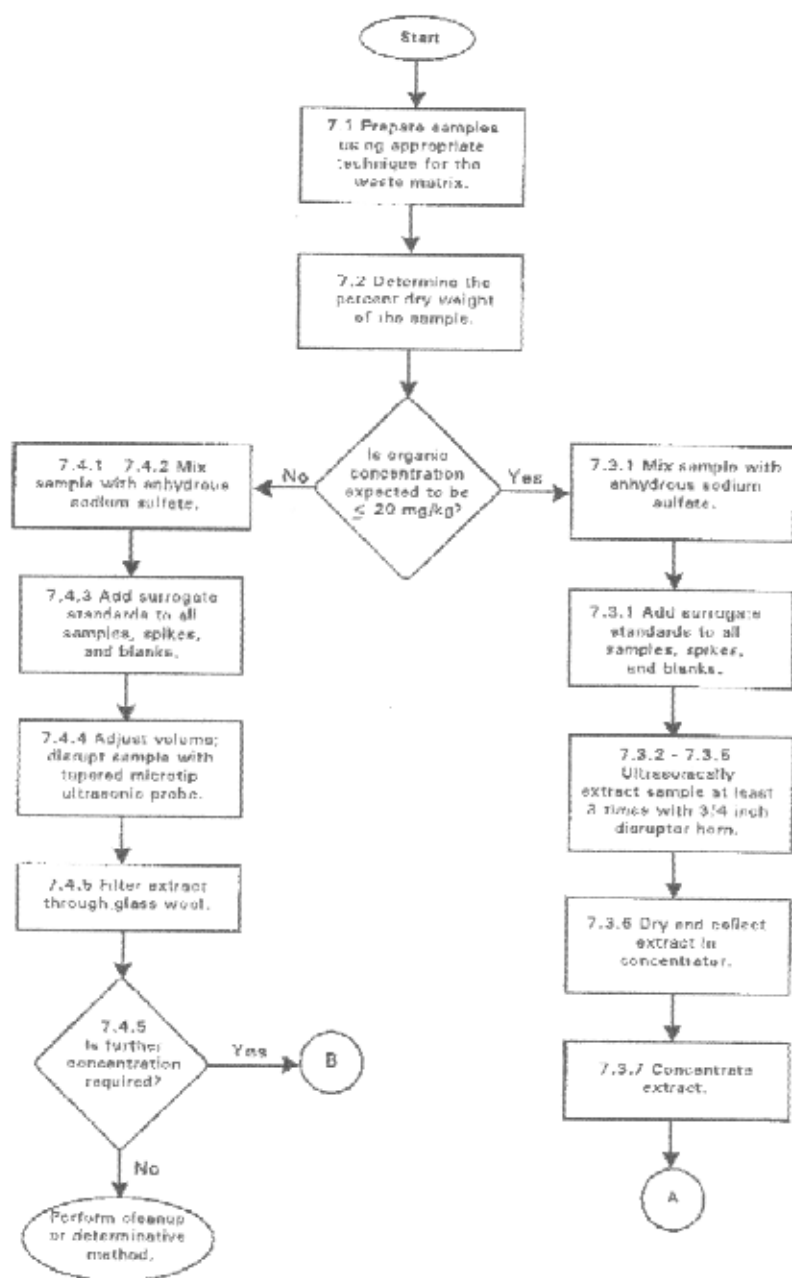
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL) ^a
8041	as received	2-propanol	hexane	1.0	1.0, 0.5 ^b
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8091	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8111	as received	hexane	hexane	2.0	10.0
8121	as received	hexane	hexane	2.0	1.0
8141	as received	hexane	hexane	10.0	10.0
8270 ^c	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0
8321	as received	methanol	-	-	1.0
8325	as received	methanol	-	-	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

^a For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

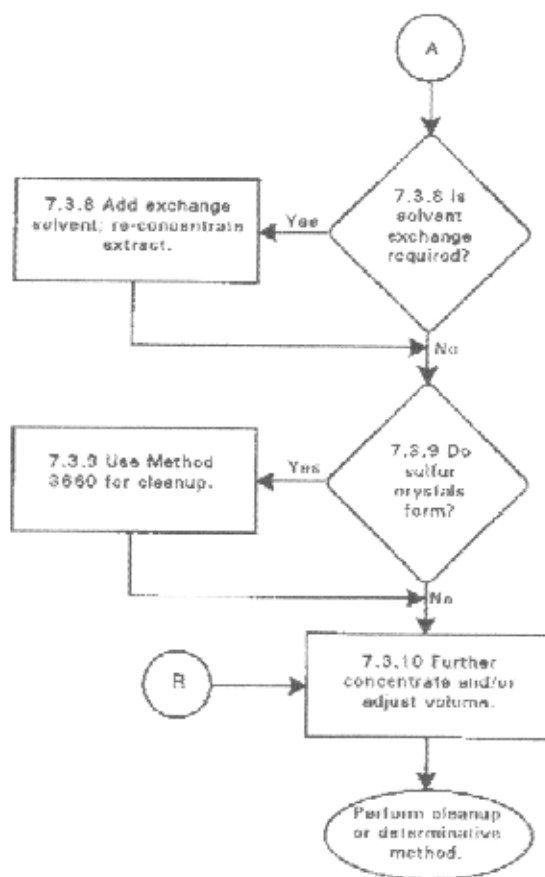
^b Phenols may be analyzed by Method 8041, using a 1.0-mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5-mL hexane extract to be analyzed by GC/ECD.

^c The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3550B
ULTRASONIC EXTRACTION



METHOD 3550B
continued



Analytical Methods
Semivolatile Organics
8270C

METHOD 8270C

SEMIVOLATILE ORGANIC COMPOUNDS
BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

Compounds	CAS No ^a	<u>Appropriate Preparation Techniques^b</u>				
		3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d ₁₀ (IS)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X

Compounds	CAS No ^a	Appropriate Preparation Techniques ^b				
		3510	3520	3540/ 3541	3550	3580
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d ₁₂ (IS)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxypfos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X

Appropriate Preparation Techniques^b

Compounds	CAS No ^a	3510	3520	3540/ 3541	3550	3580
2,4-Diaminotoluene	95-80-7	DC,OE(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d ₄ (IS)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorvos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,OS(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X

Compounds	CAS No ^a	Appropriate Preparation Techniques ^b				
		3510	3520	3540/ 3541	3550	3580
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR

Appropriate Preparation Techniques^b

Compounds	CAS No ^a	3510	3520	3540/ 3541	3550	3580
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d ₈ (IS)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d ₅ (surr)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-n-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramidate	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X

Appropriate Preparation Techniques^b

Compounds	CAS No ^a	3510	3520	3540/ 3541	3550	3580
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d ₁₂ (IS)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d ₁₀ (IS)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d ₆ (surr)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW,OS(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d ₁₄ (surr)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X

Compounds	CAS No ^a	Appropriate Preparation Techniques ^b				
		3510	3520	3540/ 3541	3550	3580
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,O,O-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

^a Chemical Abstract Service Registry Number

^b See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

- IS = This compound may be used as an internal standard.
- surr = This compound may be used as a surrogate.
- AW = Adsorption to walls of glassware during extraction and storage.
- CP = Nonreproducible chromatographic performance.
- DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
- HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
- HS = Hydrolysis during storage (number in parenthesis is percent stability).
- LR = Low response.
- ND = Not determined.
- OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
- OS = Oxidation during storage (number in parenthesis is percent stability).
- X = Greater than 70 percent recovery by this technique.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (Table 11 contains surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (Table 12 contains performance data), and Method 3561 describes a supercritical fluid extraction of solids for PAHs (see Tables 13, 14, and 15 for performance data).

1.3 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, Method 8270 is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. Refer to Sec. 7.0 of Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α -BHC, γ -BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.4.6 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.7 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4.8 Toluene diisocyanate rapidly hydrolyses in water (half-life of less than 30 min.). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.9 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 660 $\mu\text{g/kg}$ (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 $\mu\text{g/L}$ for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 μ m film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer

4.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 3 when 1 μ L of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria in Table 3 when 5 or 50 ng are introduced.

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.1.6 Guard column (optional) - (J&W Deactivated Fused Silica, 0.25 mm ID x 6 m, or equivalent) between the injection port and the analytical column joined with column joiners (Hewlett-Packard Catalog No. 5062-3556, or equivalent).

4.2 Syringe - 10- μ L.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.0001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.3.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.3.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂ (see Table 5). Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met.

5.4.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d₁₂. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at -10°C or less when not in use. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.4.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at -10°C or less when not in use. If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method.

5.6.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.6.2 Each 1-mL aliquot of calibration standard should be spiked with 10 μ L of the internal standard solution prior to analysis. All standards should be stored at -10°C or less, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration verification standard should be prepared weekly and stored at 4°C. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7 Surrogate standards - The recommended surrogates are phenol-d₆, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d₅, 2-fluorobiphenyl, and p-terphenyl-d₁₄. See Method 3500 for instructions on preparing the surrogate solutions.

5.7.1 Surrogate Standard Check: Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

5.7.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute surrogate solution may be necessary.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS).

5.8.1 Matrix Spike Check: Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

5.8.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute matrix and LCS spiking solution may be necessary.

5.8.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking

standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Store the sample extracts at -10°C, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

<u>Matrix</u>	<u>Methods</u>
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

7.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L). Therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

<u>Analytes of interest</u>	<u>Methods</u>
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041 ^a
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620

<u>Analytes of interest</u>	<u>Methods</u>
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

^a Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene elutes
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

7.3.1.2 Use the DFTPP mass intensity criteria in Table 3 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD

should not exceed 20%. (See Sec. 8.0 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

7.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column. The use of a guard column (Sec. 4.1.6) between the injection port and the analytical column may help prolong analytical column performance.

7.3.2 The internal standards selected in Sec. 5.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene- d_4 , use 152 m/z for quantitation).

7.3.3 Analyze 1-2 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 5.6 and Method 8000). The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

Calculate response factors (RFs) for each target analyte relative to one of the internal standards as follows:

$$\text{RF} = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate, in $\mu\text{g/L}$.

C_{is} = Concentration of the internal standard, in $\mu\text{g/L}$.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.

7.3.4.2 The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC (see Table 4) must be less than or equal to 30%.

$$\text{mean RF} = \overline{\text{RF}} = \frac{\sum_{i=1}^n \text{RF}_i}{n}$$
$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n (\text{RF}_i - \overline{\text{RF}})^2}{n-1}}$$

$$\text{RSD} = \frac{\text{SD}}{\overline{\text{RF}}} \times 100$$

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.5.4 If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

7.3.7 Linearity of target analytes - If the RSD of any target analytes is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.7.1 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 in Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 designates a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8270 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000B for method blank performance criteria.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration check compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Table 4 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference for each CCC is less than or equal to 20%, then the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project,

and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 μL of the internal standard solution to the 1-mL concentrated sample extract obtained from sample preparation.

7.5.3 Inject a 1-2 μL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 7.3). The volume to be injected should contain 100 ng of base/neutral and 200 ng of acid surrogates (assuming 100% recovery), unless a more sensitive GC/MS system is being used and the surrogate solution is less concentrated than that listed in Sec. 5.7. The injection volume must be the same volume used for the calibration standards.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/ μL , unless a more sensitive GC/MS system is being used).

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. However, SIM

may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be identified, quantitated and reported as the sum of both compounds by the GC.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the

analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

- (1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- (2) The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)
- (3) Molecular ions present in the reference spectrum should be present in the sample spectrum.
- (4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- (5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 7.3.5). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_s should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, by Methods 8081 or 8082. However, Method 8270 may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/ μ L in the concentrated sample extract.

7.7.6 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are quantitated as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be summed and reported as the sum of both compounds.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Sec. 7.0 of Method 8000 and include calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8270:

8.2.1 The GC/MS system must be tuned to meet the DFTPP criteria listed in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the calibration verification acceptance criteria in Sec. 7.4, each 12 hours.

8.2.4 The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 7.6.1.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed, a septum is changed), see the guidance in Sec 8.2 of Method 8000 regarding whether recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations ranging from 5 to 1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7. These values are presented as guidance only and are not intended as absolute acceptance criteria. Laboratories should generate their own acceptance criteria for capillary column method performance. (See Method 8000.)

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 8.

9.3 Method performance data (using Method 3541 Automated Soxhlet extraction) are presented in Table 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 10 and were taken from Reference 7.

9.4 Surrogate precision and accuracy data are presented in Table 11 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by Method 8270.

9.5 Single laboratory precision and bias data (using Method 3545 Accelerated Solvent Extraction) for semivolatile organic compounds are presented in Table 12. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by Perstorp Environmental Soxtec™ (automated Soxhlet). The data presented in Table 12 represents seven replicate extractions and analyses for each individual sample and were taken from reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low-101.2%, mid-97.2% and high-99.2%.

9.6 Single laboratory precision and bias data (using Method 3561 SFE Extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (one, EC-1, a lake sediment from Environment Canada and the other, HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 13 and 14 and were taken from Reference 10.

9.7 Single laboratory precision and accuracy data (using Method 3561 SFE Extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO₂; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in Table 15 and were taken from Reference 11.

10.0 REFERENCES

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TABLE 1
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75 ^a	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d ₄ (IS)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	44,45,74
Thiophenol (Benzenethiol)	7.42	110	66,109,84
Methyl methanesulfonate	7.48	80	79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	79,95,109,140
Ethyl methanesulfonate	9.62	79	109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d ₈ (IS)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	155,127,81,109
Diethyl sulfate	11.37	139	45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	108,77,79,90
Hexachloropropene	12.45	213	211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	41,42,68,69
Acetophenone	12.67	105	71,51,120
4-Methylphenol	12.82	107	108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	107,77,51,79
3-Methylphenol	12.93	107	108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,55,56,41
1,4-Phenylenediamine	13.62	108	80,53,54,52
1-Chloronaphthalene	13.65 ^a	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	76,50,148
o-Anisidine	15.00	108	80,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d ₁₀ (IS)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	164,126,98,63
4-Chloroaniline	15.50	127	129,65,92
Isosafrole	15.60	162	131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00 ^a	143	115,116
1,4-Naphthoquinone	16.23	158	104,102,76,50,130
p-Cresidine	16.45	122	94,137,77,93
Dichlorovos	16.48	109	185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	135,134,91,77
N-Nitrosodi-n-butylamine	16.73	84	57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	104,77,103,135

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramidate	17.33	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	127,129,65,39
Diphenylamine	17.54 ^a	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	214,179,108,143,218
1-Naphthylamine	18.20	143	115,89,63
1-Acetyl-2-thiourea	18.22	118	43,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,79,106,94
Thionazine	19.35	107	96,97,143,79,68
4-Nitroaniline	19.37	138	65,108,92,80,39
Phenanthrene-d ₁₀ (IS)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	75,50,76,92,122
Mevinphos	19.90	127	192,109,67,164
Naled	20.03	109	145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	76,50,75,92,122
Diallate (cis or trans)	20.57	86	234,43,70
1,2-Dinitrobenzene	20.58	168	50,63,74
Diallate (trans or cis)	20.78	86	234,43,70
Pentachlorobenzene	21.35	250	252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	79,52,138,153,77
Pentachloronitrobenzene	21.72	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	131,230,166,234,168
Dihydrosaffrole	22.42	135	64,77
Demeton-O	22.72	88	89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	74,213,120,91,63
Dicrotophos	23.82	127	67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	43,264,41,290
Bromoxynil	23.90	277	279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	192,67,97,109
Phorate	24.10	75	121,97,93,260

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Sulfallate	24.23	188	88,72,60,44
Demeton-S	24.30	88	60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	93,125,143,229
Phenobarbital	24.70	204	117,232,146,161
Carbofuran	24.90	164	149,131,122
Octamethyl pyrophosphoramidate	24.95	135	44,199,286,153,243
4-Aminobiphenyl	25.08	169	168,170,115
Dioxathion	25.25	97	125,270,153
Terbufos	25.35	231	57,97,153,103
α,α -Dimethylphenylamine	25.43	58	91,65,134,42
Pronamide	25.48	173	175,145,109,147
Aminoazobenzene	25.72	197	92,120,65,77
Dichlone	25.77	191	163,226,228,135,193
Dinoseb	25.83	211	163,147,117,240
Disulfoton	25.83	88	97,89,142,186
Fluchloralin	25.88	306	63,326,328,264,65
Mexacarbate	26.02	165	150,134,164,222
4,4'-Oxydianiline	26.08	200	108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	152,141,169,151
Phosphamidon	26.85	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	185,41,193,266
Methyl parathion	27.03	109	125,263,79,93
Carbaryl	27.17	144	115,116,201
Dimethylaminoazobenzene	27.50	225	120,77,105,148,42
Propylthiouracil	27.68	170	142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d ₁₂ (IS)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	125,127,93,158
Kepone	28.18	272	274,237,178,143,270
Fenthion	28.37	278	125,109,169,153
Parathion	28.40	109	97,291,139,155
Anilazine	28.47	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	106,196,180
Carbophenothion	28.58	157	97,121,342,159,199
5-Nitroacenaphthene	28.73	199	152,169,141,115
Methapyrilene	28.77	97	50,191,71
Isodrin	28.95	193	66,195,263,265,147

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Captan	29.47	79	149,77,119,117
Chlorfenvinphos	29.53	267	269,323,325,295
Crotoxyphos	29.73	127	105,193,166
Phosmet	30.03	160	77,93,317,76
EPN	30.11	157	169,185,141,323
Tetrachlorvinphos	30.27	329	109,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	167,195
Barban	30.83	222	51,87,224,257,153
Aramite	30.92	185	191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	139,253,111,141
Fensulfothion	31.87	293	97,308,125,292
Ethion	32.08	231	97,153,125,121
Diethylstilbestrol	32.15	268	145,107,239,121,159
Famphur	32.67	218	125,93,109,217
Tri-p-tolyl phosphate ^b	32.75	368	367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d ₁₂ (IS)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	241,239,120
5,5-Diphenylhydantoin	33.40	180	104,252,223,209
Captafol	33.47	79	77,80,107
Dinocap	33.47	69	41,39
Methoxychlor	33.55	227	228,152,114,274,212
2-Acetylaminofluorene	33.58	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	201,229
3-Methylcholanthrene	35.07	268	252,253,126,134,113
Phosalone	35.23	182	184,367,121,379
Azinphos-methyl	35.25	160	132,93,104,105
Leptophos	35.28	171	377,375,77,155,379
Mirex	35.43	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,119,217,219,199
Dibenz(a,j)acridine	36.40	279	280,277,250
Mestranol	36.48	277	310,174,147,242
Coumaphos	37.08	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	151,150,300

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	135,105,77
Hexachlorophene	47.98	196	198,209,211,406,408
Aldrin	--	66	263,220
Aroclor 1016	--	222	260,292
Aroclor 1221	--	190	224,260
Aroclor 1232	--	190	224,260
Aroclor 1242	--	222	256,292
Aroclor 1248	--	292	362,326
Aroclor 1254	--	292	362,326
Aroclor 1260	--	360	362,394
α -BHC	--	183	181,109
β -BHC	--	181	183,109
δ -BHC	--	183	181,109
γ -BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237,165
4,4'-DDE	--	246	248,176
4,4'-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
Endosulfan I	--	195	339,341
Endosulfan II	--	337	339,341
Endosulfan sulfate	--	272	387,422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr)	--	172	171
2-Fluorophenol (surr)	--	112	64
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d ₅ (surr)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d ₆ (surr)	--	99	42,71
Terphenyl-d ₁₄ (surr)	--	244	122,212
2,4,6-Tribromophenol (surr)	--	330	332,141
Toxaphene	--	159	231,233

IS = internal standard

surr = surrogate

^aEstimated retention times

^bSubstitute for the non-specific mixture, tricresyl phosphate

TABLE 2

ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

Compound	Estimated Quantitation Limits ^a	
	Ground water µg/L	Low Soil/Sediment ^b µg/kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits ^a	
	Ground water µg/L	Low Soil/Sediment ^b µg/kg
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits ^a	
	Ground water µg/L	Low Soil/Sediment ^b µg/kg
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits ^a	
	Ground water µg/L	Low Soil/Sediment ^b µg/kg
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramidate	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits ^a	
	Ground water µg/L	Low Soil/Sediment ^b µg/kg
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
O,O,O-Triethyl phosphorothioate	NT	ND

^a Sample EQLs are highly matrix-dependent. The EQLs listed here are provided for guidance and may not always be achievable.

^b EQLs listed for soil/sediment are based on wet weight. Normally, data are reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. These EQLs are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined

NA = Not Applicable

NT = Not Tested

Other Matrices

Factor^c

High-concentration soil and sludges by ultrasonic extractor

7.5

Non-water miscible waste

75

^cEQL = (EQL for Low Soil/Sediment given above in Table 2) x (Factor)

TABLE 3
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA^{a,b}

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

^a Data taken from Reference 3.

^b Alternate tuning criteria may be used, (e.g., CLP, Method 525, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 4
CALIBRATION CHECK COMPOUNDS (CCC)

<u>Base/Neutral Fraction</u>	<u>Acid Fraction</u>
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d ₄	Naphthalene-d ₈	Acenaphthene-d ₁₀
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α -Dimethylphenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene-d ₈ (surr)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d ₈ (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d ₁₀	Chrysene-d ₁₂	Perylene-d ₁₂
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	
Hexachlorobenzene	Pyrene	
N-Nitrosodiphenylamine	Terphenyl-d ₄ (surr)	
Pentachlorophenol	7,12-Dimethylbenz-(a)anthracene	
Pentachloronitrobenzene	Di-n-octyl phthalate	
Phenacetin	Indeno(1,2,3-cd)pyrene	
Phenanthrene	3-Methylcholanthrene	
Pronamide		

(surr) = surrogate

TABLE 6
MULTILABORATORY PERFORMANCE DATA^a

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for \bar{x} (µg/L)	Range p, p _s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192

TABLE 6
(continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for \bar{x} (µg/L)	Range p, p _s (%)
Heptachlor epoxide	100	54.7	70.9-109.4	26-155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Aroclor 1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L

\bar{x} = Average recovery for four recovery measurements, in µg/L

p, p_s = Measured percent recovery

D = Detected; result must be greater than zero

^a Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION^a

Compound	Accuracy, as recovery, x' ($\mu\text{g/L}$)	Single analyst precision, s' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Acenaphthene	0.96C+0.19	0.15 \bar{x} -0.12	0.21 \bar{x} -0.67
Acenaphthylene	0.89C+0.74	0.24 \bar{x} -1.06	0.26 \bar{x} -0.54
Aldrin	0.78C+1.66	0.27 \bar{x} -1.28	0.43 \bar{x} +1.13
Anthracene	0.80C+0.68	0.21 \bar{x} -0.32	0.27 \bar{x} -0.64
Benz(a)anthracene	0.88C-0.60	0.15 \bar{x} +0.93	0.26 \bar{x} -0.21
Benzo(b)fluoranthene	0.93C-1.80	0.22 \bar{x} +0.43	0.29 \bar{x} +0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19 \bar{x} +1.03	0.35 \bar{x} +0.40
Benzo(a)pyrene	0.90C-0.13	0.22 \bar{x} +0.48	0.32 \bar{x} +1.35
Benzo(g,h,i)perylene	0.98C-0.86	0.29 \bar{x} +2.40	0.51 \bar{x} -0.44
Benzyl butyl phthalate	0.66C-1.68	0.18 \bar{x} +0.94	0.53 \bar{x} +0.92
β -BHC	0.87C-0.94	0.20 \bar{x} -0.58	0.30 \bar{x} +1.94
δ -BHC	0.29C-1.09	0.34 \bar{x} +0.86	0.93 \bar{x} -0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35 \bar{x} -0.99	0.35 \bar{x} +0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16 \bar{x} +1.34	0.26 \bar{x} +2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24 \bar{x} +0.28	0.25 \bar{x} +1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26 \bar{x} +0.73	0.36 \bar{x} +0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13 \bar{x} +0.66	0.16 \bar{x} +0.66
2-Chloronaphthalene	0.89C+0.01	0.07 \bar{x} +0.52	0.13 \bar{x} +0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 \bar{x} -0.94	0.30 \bar{x} -0.46
Chrysene	0.93C-1.00	0.28 \bar{x} +0.13	0.33 \bar{x} -0.09
4,4'-DDD	0.56C-0.40	0.29 \bar{x} -0.32	0.66 \bar{x} -0.96
4,4'-DDE	0.70C-0.54	0.26 \bar{x} -1.17	0.39 \bar{x} -1.04
4,4'-DDT	0.79C-3.28	0.42 \bar{x} +0.19	0.65 \bar{x} -0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30 \bar{x} +8.51	0.59 \bar{x} +0.25
Di-n-butyl phthalate	0.59C+0.71	0.13 \bar{x} +1.16	0.39 \bar{x} +0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20 \bar{x} +0.47	0.24 \bar{x} +0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25 \bar{x} +0.68	0.41 \bar{x} +0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24 \bar{x} +0.23	0.29 \bar{x} +0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28 \bar{x} +7.33	0.47 \bar{x} +3.45
Dieldrin	0.82C-0.16	0.20 \bar{x} -0.16	0.26 \bar{x} -0.07
Diethyl phthalate	0.43C+1.00	0.28 \bar{x} +1.44	0.52 \bar{x} +0.22
Dimethyl phthalate	0.20C+1.03	0.54 \bar{x} +0.19	1.05 \bar{x} -0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12 \bar{x} +1.06	0.21 \bar{x} +1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14 \bar{x} +1.26	0.19 \bar{x} +0.35
Di-n-octyl phthalate	0.76C-0.79	0.21 \bar{x} +1.19	0.37 \bar{x} +1.19
Endosulfan sulfate	0.39C+0.41	0.12 \bar{x} +2.47	0.63 \bar{x} -1.03
Endrin aldehyde	0.76C-3.86	0.18 \bar{x} +3.91	0.73 \bar{x} -0.62
Fluoranthene	0.81C+1.10	0.22 \bar{x} -0.73	0.28 \bar{x} -0.60
Fluorene	0.90C-0.00	0.12 \bar{x} +0.26	0.13 \bar{x} +0.61
Heptachlor	0.87C-2.97	0.24 \bar{x} -0.56	0.50 \bar{x} -0.23
Heptachlor epoxide	0.92C-1.87	0.33 \bar{x} -0.46	0.28 \bar{x} +0.64

TABLE 7
(continued)

Compound	Accuracy, as recovery, x' ($\mu\text{g/L}$)	Single analyst precision, s_r' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Hexachlorobenzene	$0.74C+0.66$	$0.18\bar{x}-0.10$	$0.43\bar{x}-0.52$
Hexachlorobutadiene	$0.71C-1.01$	$0.19\bar{x}+0.92$	$0.26\bar{x}+0.49$
Hexachloroethane	$0.73C-0.83$	$0.17\bar{x}+0.67$	$0.17\bar{x}+0.80$
Indeno(1,2,3-cd)pyrene	$0.78C-3.10$	$0.29\bar{x}+1.46$	$0.50\bar{x}-0.44$
Isophorone	$1.12C+1.41$	$0.27\bar{x}+0.77$	$0.33\bar{x}+0.26$
Naphthalene	$0.76C+1.58$	$0.21\bar{x}-0.41$	$0.30\bar{x}-0.68$
Nitrobenzene	$1.09C-3.05$	$0.19\bar{x}+0.92$	$0.27\bar{x}+0.21$
N-Nitrosodi-n-propylamine	$1.12C-6.22$	$0.27\bar{x}+0.68$	$0.44\bar{x}+0.47$
Aroclor 1260	$0.81C-10.86$	$0.35\bar{x}+3.61$	$0.43\bar{x}+1.82$
Phenanthrene	$0.87C+0.06$	$0.12\bar{x}+0.57$	$0.15\bar{x}+0.25$
Pyrene	$0.84C-0.16$	$0.16\bar{x}+0.06$	$0.15\bar{x}+0.31$
1,2,4-Trichlorobenzene	$0.94C-0.79$	$0.15\bar{x}+0.85$	$0.21\bar{x}+0.39$
4-Chloro-3-methylphenol	$0.84C+0.35$	$0.23\bar{x}+0.75$	$0.29\bar{x}+1.31$
2-Chlorophenol	$0.78C+0.29$	$0.18\bar{x}+1.46$	$0.28\bar{x}+0.97$
2,4-Dichlorophenol	$0.87C-0.13$	$0.15\bar{x}+1.25$	$0.21\bar{x}+1.28$
2,4-Dimethylphenol	$0.71C+4.41$	$0.16\bar{x}+1.21$	$0.22\bar{x}+1.31$
2,4-Dinitrophenol	$0.81C-18.04$	$0.38\bar{x}+2.36$	$0.42\bar{x}+26.29$
2-Methyl-4,6-dinitrophenol	$1.04C-28.04$	$0.10\bar{x}+42.29$	$0.26\bar{x}+23.10$
2-Nitrophenol	$0.07C-1.15$	$0.16\bar{x}+1.94$	$0.27\bar{x}+2.60$
4-Nitrophenol	$0.61C-1.22$	$0.38\bar{x}+2.57$	$0.44\bar{x}+3.24$
Pentachlorophenol	$0.93C+1.99$	$0.24\bar{x}+3.03$	$0.30\bar{x}+4.33$
Phenol	$0.43C+1.26$	$0.26\bar{x}+0.73$	$0.35\bar{x}+0.58$
2,4,6-Trichlorophenol	$0.91C-0.18$	$0.16\bar{x}+2.22$	$0.22\bar{x}+1.81$

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of \bar{x} , in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{x} , in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

\bar{x} = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

^a Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 8
EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

Compound	Percent Recovery on Day 0		Percent Recovery on Day 7	
	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 9

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANICS
FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION
(METHOD 3541) WITH HEXANE-ACETONE (1:1)^a

Compound	Clay Soil		Topsoil	
	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

^a The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 10

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION
OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY
AUTOMATED SOXHLET (METHOD 3541)^a

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9

TABLE 10
(continued)

Compound	Mean Recovery	RSD
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

^a Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 11
PRECISION AND BIAS VALUES FOR METHOD 3542¹

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation Percent
2-Fluorophenol	74.6	28.6	38.3
Phenol-d ₅	77.8	27.7	35.6
Nitrobenzene-d ₅	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d ₁₄	78.6	32.4	41.3

¹ The surrogate values shown in Table 11 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 12

**ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™**

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	102.0
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	101.9
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	101.6
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	120.6
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	119.2
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	112.5
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	104.7
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	100.2
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	110.3
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	98.1
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	118.6
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	100.2
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	101.7
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	109.8
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	96.3
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	97.2
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	98.6
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	84.5	137.0	99.4	95.3	104.2
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	106.1
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	108.1
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	104.7
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	99.7
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	102.1
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	75.8
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	96.9
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	94.1
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	96.2
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	92.6
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	90.3
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	101.7
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	92.9
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	98.4
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	75.6
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	90.7

TABLE 12 (cont.)

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	98.8
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	94.4
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	95.4
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	99.1
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	96.8
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	95.8
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	93.7
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	81.2
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	100.6
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	101.2
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	99.1
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	102.7
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	105.2
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	116.5
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	101.5
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	102.9
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	99.0
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	103.1
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	99.9
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	102.7
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	98.6
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	66.4
Average	95.1	94.3	101.0	95.5	96.5	104.1	113.0	100.9	92.5	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs
FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value ^a (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9) ^b	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

^a Relative standard deviations for the SFE values are based on six replicate extractions.

^b Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs
FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value ^a (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

^a Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 15

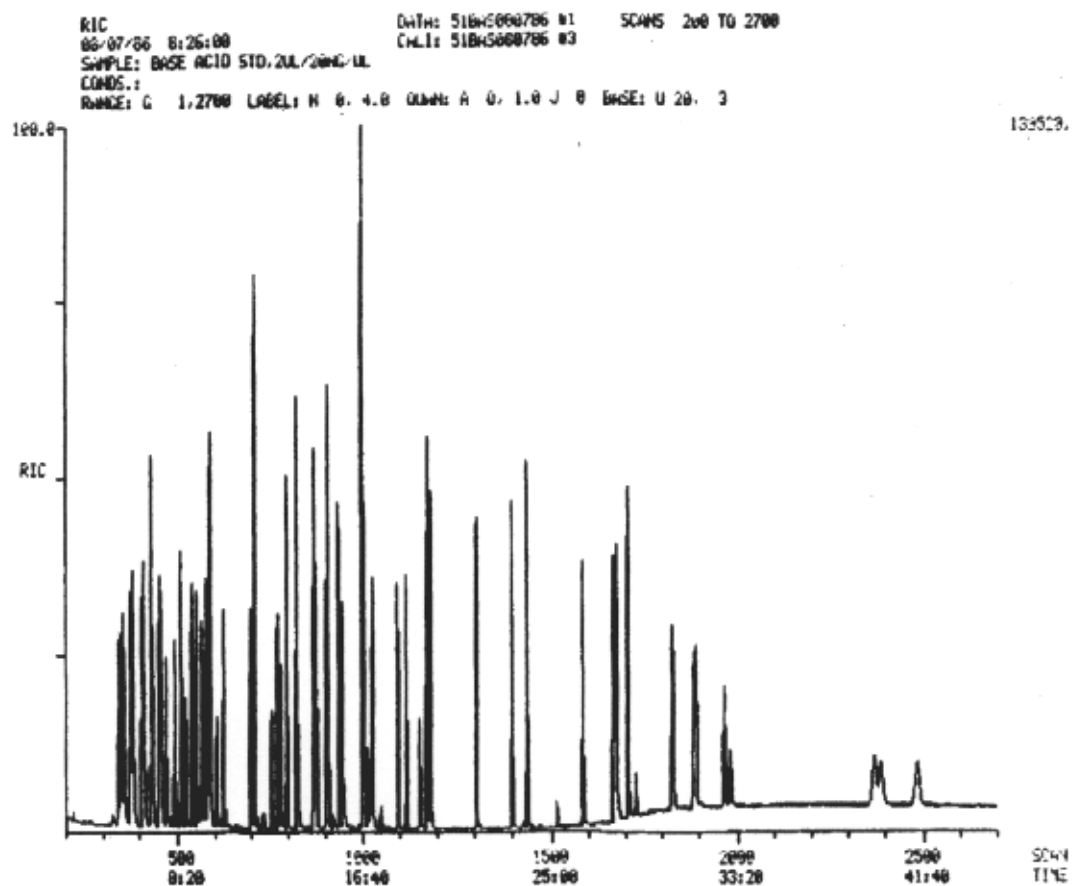
SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs
FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561
(SFE - LIQUID TRAP)

Compound	Certified Value (mg/kg)			SFE Value ^a (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4	±	8.2	29.55	91	10.5
2-Methylnaphthalene	62.1	±	11.5	76.13	122	2.0
Acenaphthene	632	±	105	577.28	91	2.9
Dibenzofuran	307	±	49	302.25	98	4.1
Fluorene	492	±	78	427.15	87	3.0
Phenanthrene	1618	±	340	1278.03	79	3.4
Anthracene	422	±	49	400.80	95	2.6
Fluoranthene	1280	±	220	1019.13	80	4.5
Pyrene	1033	±	285	911.82	88	3.1
Benz(a)anthracene	252	±	38	225.50	89	4.8
Chrysene	297	±	26	283.00	95	3.8
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153	±	22	130.88	86	10.7
Benzo(a)pyrene	97.2	±	17.1	58.28	60	6.5

^a Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

FIGURE 1
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



METHOD 8270C
SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS
SPECTROMETRY (GC/MS)

